A

Project Report

On

Synthesis and Characterization of Novel Adsorbents

Submitted by

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CERTIFICATE

It is certified that the work contained in the thesis entitled **"*Synthesis and Characterization of Novel Adsorbents*"** submitted by **Mr. Sayandeep Mitra**, has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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ABSTRACT

New materials usher new technologies. Synthesizing novel materials has long been cherished as a stepping stone in technological advancement. In our current area of research we tried to explore the concept of reticular chemistry in synthesizing 'novel' metal organic frameworks. It is however noteworthy to mention here that the term 'novel' signifies a new class of adsorbents which is popularly known as 'metal organic frameworks' or MOFs. Due to simplicity in synthesis and attractive physical properties, we picked Cr and Cu based MOFs. Cr-BDC (or, MIL-101) and Cu-BTC (or, HKUST-1) were synthesized hydrothermally in a Teflon lined stainless steel high pressure autoclave. The synthesized materials were thoroughly characterized using imaging techniques like optical microscopy and scanning electron microscopy. The materials were undergone powder X-ray diffraction analysis to understand whether they are crystalline or amorphous in nature. Thermal stability of the synthesized products was closely examined in a thermogravimetry analyzer. These characterization techniques corroborated well with the published literature data and vindicated our synthesis methods.

Additionally, new variants or derivatives of the established MOFs were tried to be synthesized by changing either the organic ligands or the synthesis conditions. A perusal of our efforts is included in the results and discussions section.

Keywords: Metal Organic Frameworks, Cu-BTC, Cr-BDC, Reticular Chemistry

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CHAPTER 1

Introduction

1.1 Novel Adsorbents

New materials usher new technologies. Synthesizing novel materials has long been cherished as a stepping stone in technological advancement. It is not long back when zeolites and activated carbon, known to be the most versatile, used primarily in wide ranging industrial applications. But as the need grows for more efficient, economical and highly specific functions, conventional adsorbents were not found effective enough to deal with such problems. Although, improved synthesis and different post-treatment procedures of zeolites and activated carbon resulted into some of their derivatives but the need of the hour was to design and synthesize materials that could be more effective.

In the quest for designing novel adsorbents, attention has been paid to develop hybrid structures involving both inorganic and organic components by employing novel synthetic routes. The general concept was to take advantage of both the metal coordination and functionalities of the organic components. The concept of reticular synthesis which can be described as the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures or networks, held together by strong bonding is found to be the key to the true design of novel solid-state materials. Researchers have envisioned that to fully realize the benefits of designing crystalline solid state frameworks the structural integrity and rigidity of the molecular building blocks must remain unaltered throughout the construction process: key feature of reticular synthesis **[1]**. The said mechanism plays a pivotal role in producing robust porous materials by connecting rigid rod-like organic

moieties with inflexible inorganic clusters acting as joints. The length and functionalities of the organic units determine the size and chemical environment of the resulting void spaces. Accordingly, the concept of 'tailor-made' materials finally realized.

Appropriate selection of starting materials can give rise to myriad of different structures. Within a short period of time a large variety of extended structures have been successfully prepared and the collection of compounds has been given various names e.g. 'co-ordination polymers', 'hybrid organic-inorganic materials', 'organic zeolite analogues' or 'metal organic frameworks'. Although each terminology signifies certain aspects of the materials it encompasses but for a solid to be truly called a 'Metal Organic Framework' or MOF, it must possess robustness implying strong bonding, assembling units are available for modification by organic synthesis and geometrically a well-defined structure **[2]**.

1.2 Research Objectives

In our current area of research we tried to explore the concept of reticular chemistry in synthesizing 'novel' metal organic frameworks. It is however noteworthy to mention here that the term 'novel' signifies a new class of adsorbents which is popularly known as 'metal organic frameworks' or MOFs. Due to simplicity in synthesis and attractive physical properties, we picked Cr and Cu based MOFs. Cr-BDC (or, MIL-101) and Cu-BTC (or, HKUST-1) were synthesized hydrothermally in a Teflon lined stainless steel high pressure autoclave. The synthesized materials were thoroughly characterized using imaging techniques like optical microscopy and scanning electron microscopy. The materials were undergone powder X-ray diffraction analysis to understand whether they are crystalline or amorphous in nature. Thermal stability of the synthesized products was closely examined in a

thermogravimetry analyzer. These characterization techniques corroborated well with the published literature data and vindicated our synthesis methods.

Additionally, new variants or derivatives of the established MOFs were tried to be synthesized by changing either the organic ligands or the synthesis conditions. A perusal of our efforts is included in the results and discussions section.

CHAPTER 2

Literature Review

2.1 Metal Organic Frameworks (MOFs)

2.1.1 Introduction

"Metal Organic Frameworks" or MOFs represent a class of novel materials that has caught the attention of researchers owing to their great diversity in structures resulting from co-ordination between inorganic metal atoms/ions and organic ligands as linkers. Proper selection of metal atoms/ions and organic linkers leads to innumerable possibilities in the co-ordination geometry with wide variation in structural architecture. A few very attractive motifs include honeycomb, brickwall, bilayer, ladder, herringbone, diamondoid, rectangular grid, and octahedral geometries [1-8]. The inorganic part in a MOF topology invariably (with a few exceptions) consists of first-row transition metals whereas organic links such as cyanide, glutamate, formate, triazole, oxalate, carboxylate, and squarates are well known [1, 3-15]. MOFs are crystalline porous solids composed of a 3-D network of metal ions held in place by multidentate organic molecules where the spatial organization of these structural units results to a system of channel and cavities in the nanometer length scale. The 'tunable matrices' or so-called 'tailor made' structures of MOFs has made it possible to design and synthesize materials meeting specific applications.

Although references cited in some review articles highlighted the concept of novel solids was introduced as early as sixties however history of these materials goes dates back (early examples are Hofmann type clathrates, Prussian-Blue type structures, and Werner complexes) but the true interest in this field of synthesizing MOFs generated decades later [16-17]. MOF-

5 was reported [18] and published in 1999. The inability of these solids to maintain permanent porosity and avoid structural rearrangements upon guest removal or guest exchange, some leading to complete collapse of the framework has an obvious shortcoming initially; MOFs exhibiting permanent porosity have been reported later. MOF-5 consisted of Zn^{2+} and 1, 4-benzenetricarboxylate. Fig. 2.1 shows the structure and topology of MOF-5.

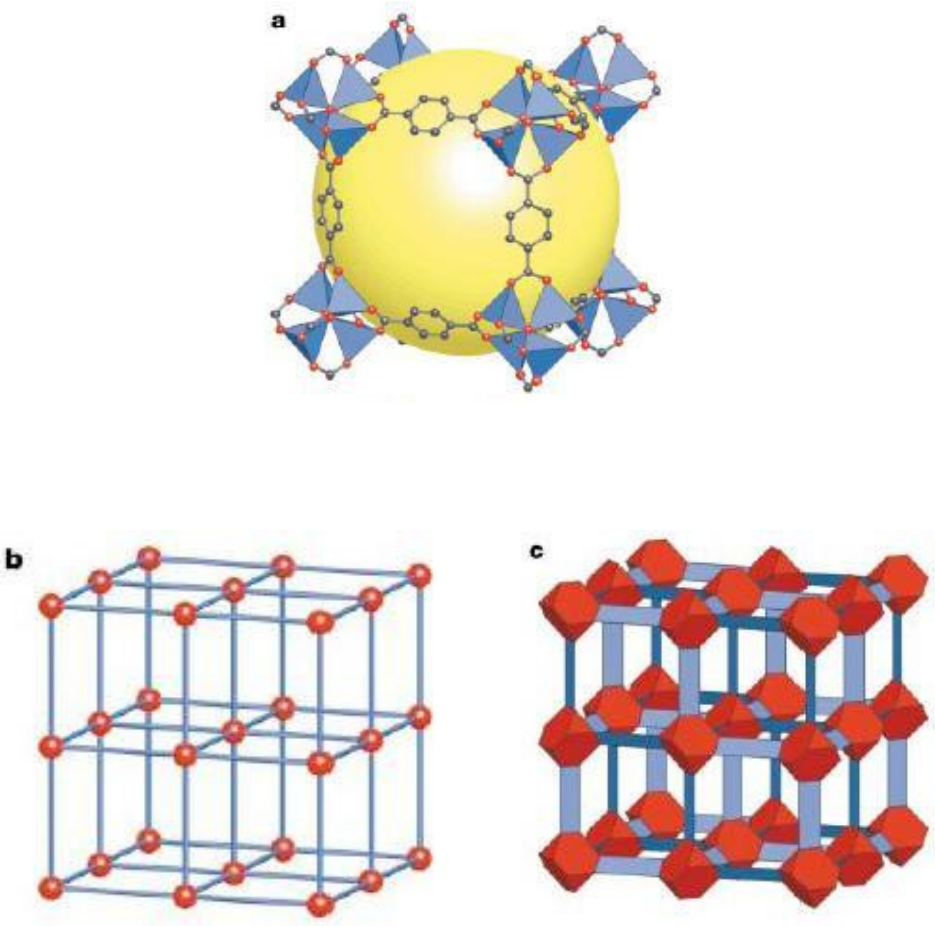

Figure 2.1: MOF-5 structure and topology. (a) The MOF-5 structure shown as ZnO_4 tetrahedra (blue polyhedral) (b) The topology of the structure shown as a ball-and-stick model (c) The structure shown as the envelopes of the (OZn4)O12 cluster (red truncated tetrahedron) and benzene dicarboxylate (BDC) ion (blue slat) [9].

In MOF-5, $Zn_4O(CO_2)_6$ units containing four ZnO_4 tetrahedra with a common vertex and six carboxylate carbon atoms that define an octahedral secondary building unit (SBU) are joined together by benzene links. This leads to a cubic network in which the vertices are the octahedral SBUs and the edges are the benzene struts. In practice, this compound was prepared from Zn(II) and BDC acid under pre-determined conditions to effect the octahedral SBU in situ. Since the SBU and the benzene links are relatively large and rigid entities, the structure produced has exceptional porosity and large micropore volume (larger than any known zeolite). The stability of the said framework is also very high. The exceptional stability of MOF-5 can be understood by comparing its basic network, composed of single atom vertices (Fig. 2.1(b)) with the actual structure of MOF-5 (Fig. 2.1(a)) which has cationic clusters at the vertices. The basic network has no resistance to shear if the links are considered to be universal joints. However, in actual MOF-5 structure, the cationic cluster has a truncated tetrahedral envelop (Fig. 2.1(c)), and the rigidly planar $O_2C\text{-}C_6H_4\text{-}CO_2$ linkers have a planar slat envelop. The linkage of these two groups produces an inherently rigid structure held together by mutually perpendicular hinges.

2.1.2 Strategies for Construction of MOF Structures

The key to successfully designing metal organic frameworks lies in the use of linkers meant to achieve desired network topologies by connecting transition-metal centers or polynuclear clusters serving as nodes of the network. Myriad of different possibilities are there depending on our choice of metal atoms/ions and organic linkers. Flexibility or the rigidity of the frameworks is greatly affected by the choice of organic linker in the structure. To illustrate the complete behaviour let us consider the following example [19].

In Fig: 2.2 (A), we have the assembly of a tetrahedrally co-ordinated metal center and a linear organic linker like 4,4´-bipyridine. It results in a structure with an expanded diamond topology. Each bond of the diamond network is replaced by a sequence of bonds that expands the networks and yields void space proportional to the length of the linker. In Fig. 2.2 (B) the organic linker is 1, 4-benzene dicarboxylate. It allows for the formation of an aggregate of metal ions into M-O-C clusters that generally referred as secondary building units (SBUs) which finally extends into a cube. A few inferences can be drawn from these observations.

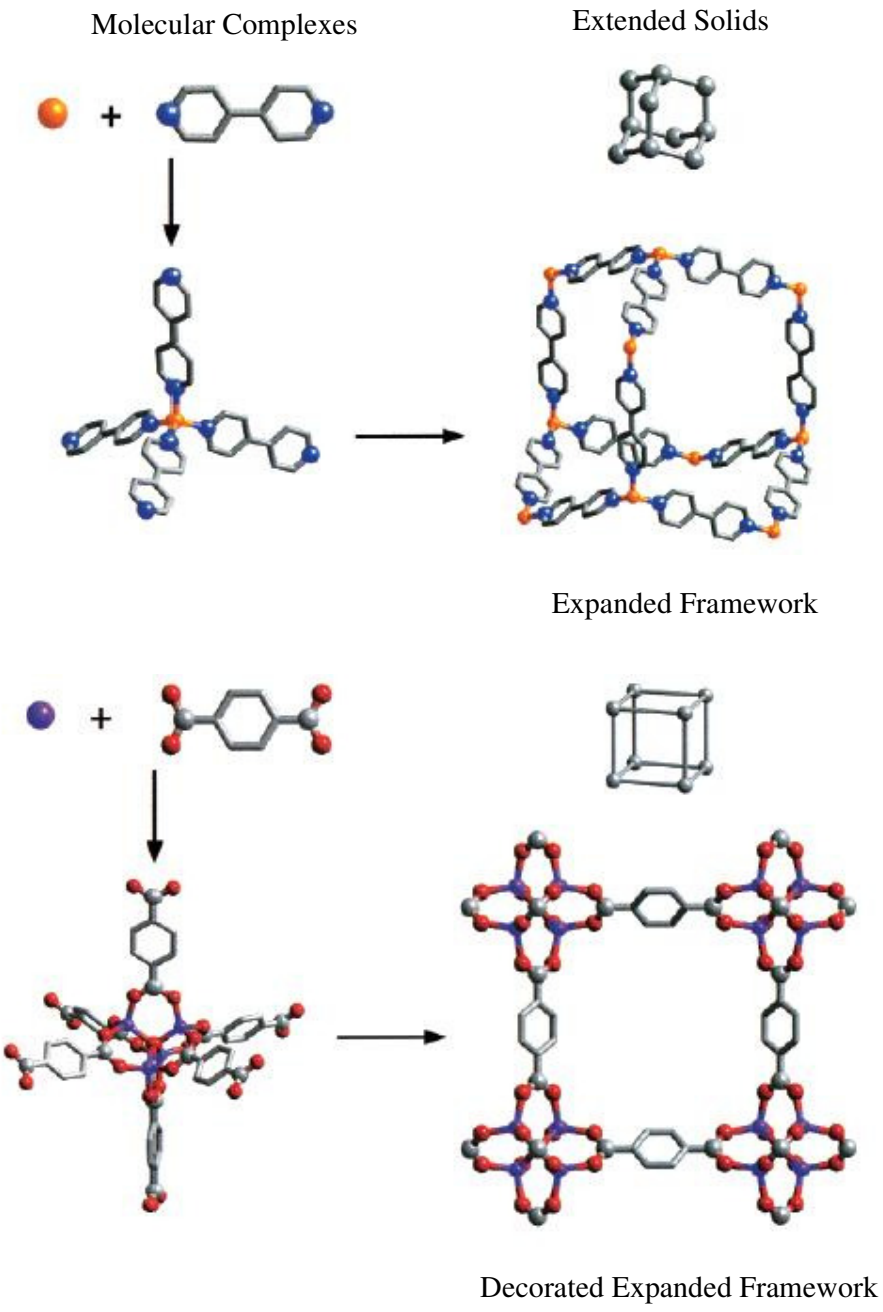

Figure 2.2: Assembly of Metal Organic Frameworks. (**A**) Flexible metal-bipyridine structures with expanded diamond topology (Metal-orange, Carbon-gray, Nitrogen-blue) (**B**) Rigid metal-carboxylate clusters expanding into a cube (Metal-purple, Carbon-gray, Oxygen-red). For the sake of clarity all hydrogen atoms are not shown [27].

(A) Aggregated metal ions or clusters in case **B** allow for the formation of a more rigid structure or frameworks since metal ions are locked into their positions by carboxylates whereas in case **A** the framework is having one metal ion at a network vertex. Thus the SBUs serve as large rigid vertices that can be joined by rigid organic links to produce extended frameworks of high structural stability.

(B) The use of long links in case **A** increase the spacing between the vertices yielding a void space proportional to the length of the linker. Although in principle such expanded structures provide large pores but often in practice they are subject to high interpenetration or interweaving leading to low porosity whereas replacement of a vertex by a group of vertices results in open structures without a tendency of interpenetration and optimal pore volume may be achieved.

So, successful synthesis of MOFs depends on the assembling of rigid molecular building blocks into ordered structures held together by strong bonds. Although variation and robustness of zeolite structures too attracted researchers to expand their range of composition beyond aluminosilicates which finally resulted into synthesizing new framework topologies and in eighties and early nineties saw the introduction of aluminophosphates, metal aluminophosphate zeotypes and many more. But the complexity in synthesis conditions where starting precursors undergo transformations (a subject not yet fully understood) together with significant trial-and-error make the complete process complicated.

Strong bonding is very essential for achieving permanent porosity in metal organic frameworks. If the bonding is weak, inter-network van der Waals interactions play a major role and only non-porous interpenetrated materials result. Thus the major challenge that needs to overcome in MOF synthesis is to ensure minimizing interpenetration sufficiently

that will help to open up pores and channels and finally to prevent the collapse of the resulting structures upon pore evacuation.

CHAPTER 3

Experimental Works

3.1 Materials

All materials were used as supplied by the vendors without further purification. The list of all the chemicals with their formula and manufacturer are shown in the respective parenthesis:

Copper (II) Nitrate trihydrate [Cu $(NO_3)_2.3H_2O$ (Merck)], 1, 3, 5-benzene tricarboxylic acid (commonly known as trimesic acid) [Merck], N, N-dimethylformamide [Merck], Ethanol [Merck] and Methanol [Merck] were used to synthesize Cu-BTC and its derivative.

Chromium (III) nitrate nonahydrate [$Cr(NO_3)_3.9H_2O$, Loba Chemie], 1,4-benzene dicarboxylic acid [$C_8H_6O_4$, Loba Chemie], Hydrofluoric acid [HF, Merck] were used as received to synthesize Cr-BDC and its derivative.

3.2 Synthesis Procedure

3.2.1 Synthesis of Cu-BTC (or, HKUST-1)

This method was taken from the work of Wang et al. [21]; they have optimized the original synthesis procedure reported by Chui et al. [20] and Yaghi et al. [22]. Benzene-1,3,5-tricarboxylic acid (1.9664 g, 0.009 mol) was added to ethanol (20ml) and mixed thoroughly, until it was completely dissolved. Cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$; 4.48 g, 0.018 mol) was dissolved into deionized water (10ml) in another flask. The two solutions were then mixed and stirred at room temperature for 16 hours. The resulting viscous mixture was transferred into a Teflon lined stainless steel autoclave. The autoclave was heated inside a hot air oven at 413 K for 48 hours. The reaction vessel was then cooled naturally to room

temperature. Blue crystals of Cu-BTC were recovered by filtration and washed thoroughly with deionized water. This product was dried at 358 K overnight.

3.2.2 Synthesis of Cu-BDC

The synthesis route was absolutely the same except the fact that the organic ligand was changed from benzene tri-carboxylic acid to benzene di-carboxylic acid.

3.2.3 Synthesis of Cr-BDC (or, MIL-101)

The original synthesis procedure was already reported elsewhere [26]. $Cr(NO_3)_3.9H_2O$ [4.00 gm, 0.206M] was added and dissolved in de-ionized water [48 cm^3]. To this solution 1, 4-benzene dicarboxylic acid [1.64 gm, 0.206M] was added. The solution was stirred and to this hydrofluoric acid [0.5 cm^3] was added drop wise. The stirring was continued for approximately 15 minutes. The complete solution was then transferred to a Teflon lined stainless steel reactor and sealed. The reactor was placed inside a hot air oven at 493 K and held for 8 hours. After the reaction time, the reactor was cooled to room temperature. A fine green coloured powder was obtained as the major product; significant amounts of H_2bdc were still present in the form of needle shaped colourless crystals along with the product. To remove this impurity, contents were completely transferred into a conical flask and N, N-dimethylformamide was added incrementally with continuous shaking to dissolve H_2bdc. The product was dried at 423 K overnight.

3.2.4 Synthesis of Cr-BTC

The synthesis route was same as that for Cr-BDC with the exception that the organic ligand is changed to benzene tri-carboxylate.

3.3 Characterization

Thermal analysis of all the samples was carried out in detail in a TGA apparatus, SHIMADZU (DTG 60 H). The TGA analysis was carried in an air atmosphere with a flow rate of 45 ml min^{-1}. Before TGA analysis the sample was mounted into a 60 μL alumina crucible. The morphologies of the synthesized products were characterized using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with an energy dispersive X-ray spectrometer (EDX). The different batches of synthesized MOF samples were analyzed by comparing images taken in an optical microscope (Hund Wetzlar H600).The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite monochromatized CuKα radiation (λ=1.5406Å) in 2θ angles ranging from 5^o to 75^o with a step size of 0.05 degree and scanning rate 1 minute.

CHAPTER 4

Results and Discussions

4.1 Surface Morphology

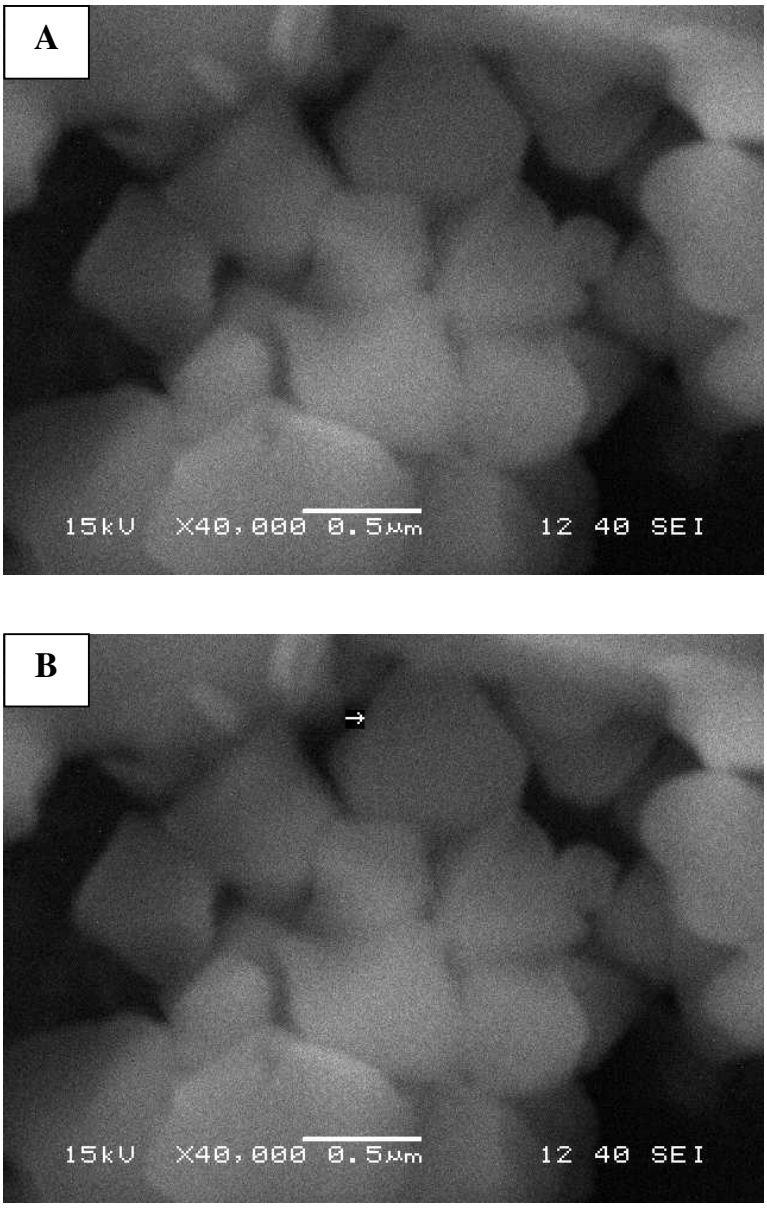

Figure 4.1: SEM images of Cr-BDC sample

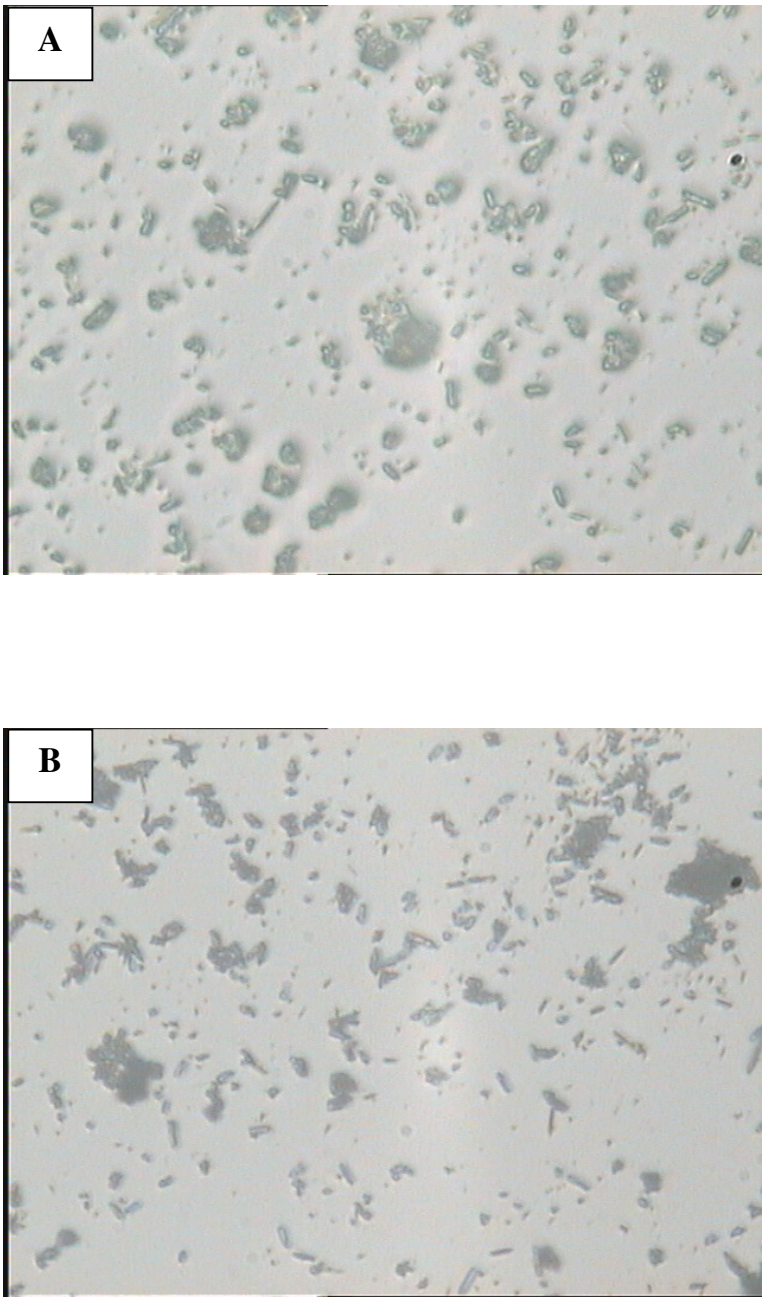

Figure 4.2: Optical microscopy images of Cr-BDC sample

Figure 4.3: Digital camera (Sony cybershot, W-35) images of Cr-BDC sample

The actual Cr-BDC sample appeared to be green to a naked eye and the digital image of a particular batch of product after final post synthesis treatment is shown in Figure 4.3. The optical microscopy images too show some cylindrical shaped green particles and a few agglomerated particles. It is however important to mention that the optical microscopy images don't show presence of any other particles apart from the green particles. This indirectly shows absence any impurity in the pure Cr-BDC sample. The morphologies of the synthesized product were characterized by using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with an energy dispersive X-ray spectrometer (EDX). The images give a clear picture about the morphology of the synthesized product. The shape of the crystallized product is octahedral in nature (Figure 4.1). The bulk of the product looks uniformly distributed with a few exceptions, where we can see large and conglomerated crystals. The agglomeration of the particles could be due to an imperfect crystallization.

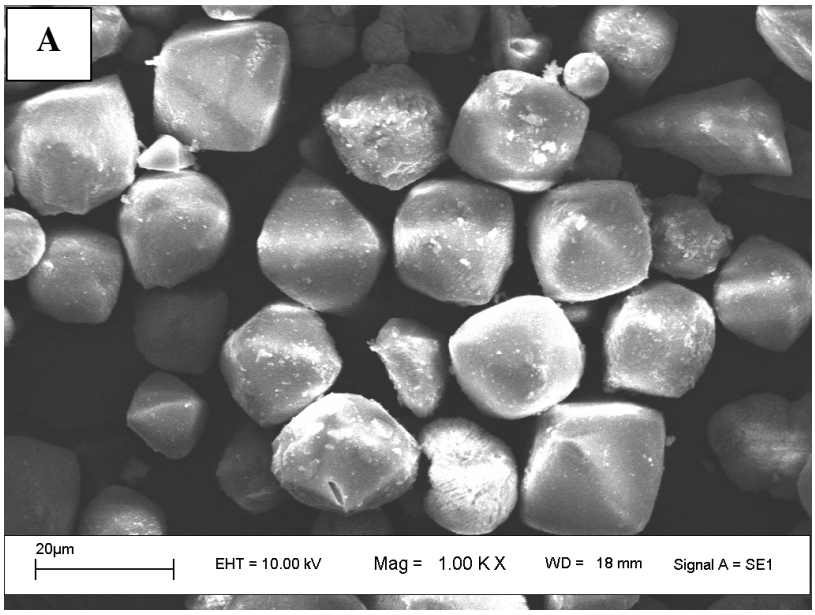

Figure 4.4: SEM image of Cu-BTC sample

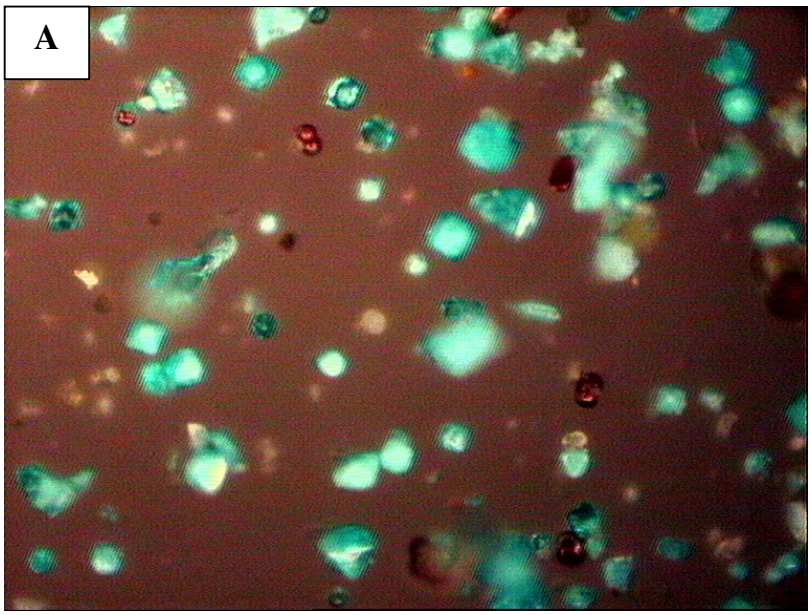

Figure 4.5: Optical microscopy image of Cu-BTC sample

The SEM image of Cu-BTC sample is shown in Figure 4.4. Unlike in case of Cr-BDC, where we can see octahedral shaped crystals, for Cu-BTC, the crystals are more spherical in nature. Although Cu-BTC samples with different surface morphologies are reported by other research groups. It is been observed that Cu-BTC samples synthesized below 100^{o}C results into octahedral shaped crystals with sharp edges.

The optical microscopy image does reveal a very interesting feature. Here, we can observe presence of red coloured spherical shaped particles along with regular Cu-BTC particles. An elaborate literature survey explained this particular scenario. Actually, at a high temperature, during synthesis of Cu-BTC, a by- product forms. This by-product is found to be Cu_2O, which is characteristically red in appearance. During synthesis of Cu-BTC, cuprous oxide acts as an impurity and has to be eliminated during post-synthesis treatment, otherwise it might deter the surface area of Cu-BTC as an adsorbent and hence it effectiveness in gas-adsorption analysis.

4.2 Powder X-ray Diffraction Patterns

Figure 4.6 and 4.7 shows the PXRD pattern of synthesized Cr-BDC and Cu-BTC samples. The obtained samples were confirmed by powder X-ray diffraction (XRD, Philips Analytical, PW-3040) by a diffractometer equipped with the graphite monochromatized CuKα radiation, λ=1.5406Å) in 2θ angles ranging from 5^{o} to 75^{o} with a step size of 0.05 and scanning rate 1 minutes. Powder XRD patterns confirm the crystallinity of both the products and corroborate well with the published literature. Although SEM images conclusively showed the formation of Cu_2O as the impurity during synthesis of Cu-BTC samples, but the XRD pattern doesn't show categorically the presence of specific peaks for that. So, we can conclude that even though impurities formed during synthesis of Cu-BTC, but its percentage is not predominant.

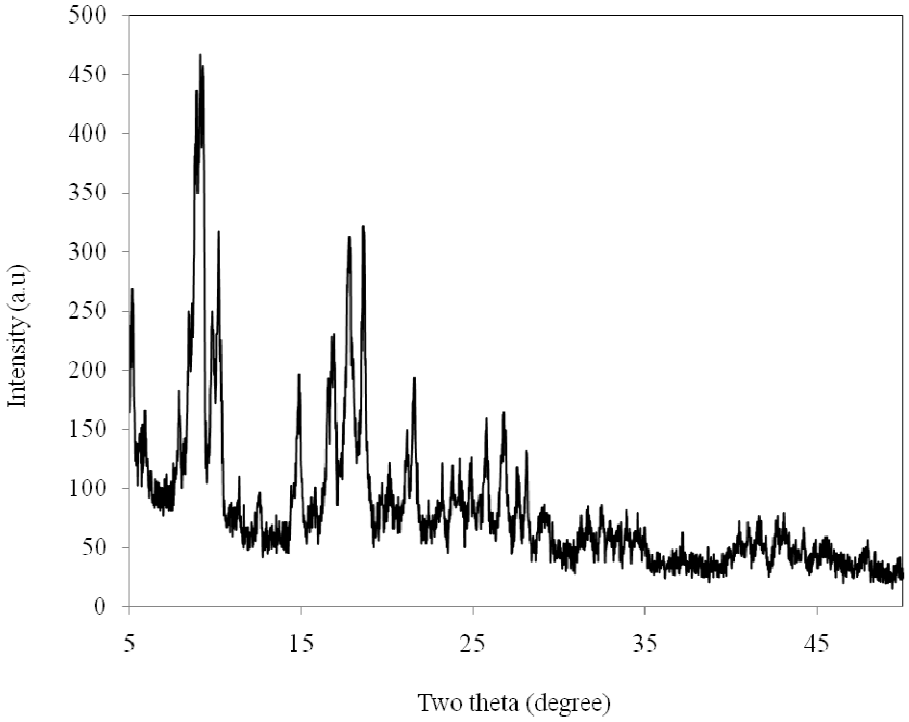

Figure 4.6: Powder XRD pattern of Cr-BDC sample

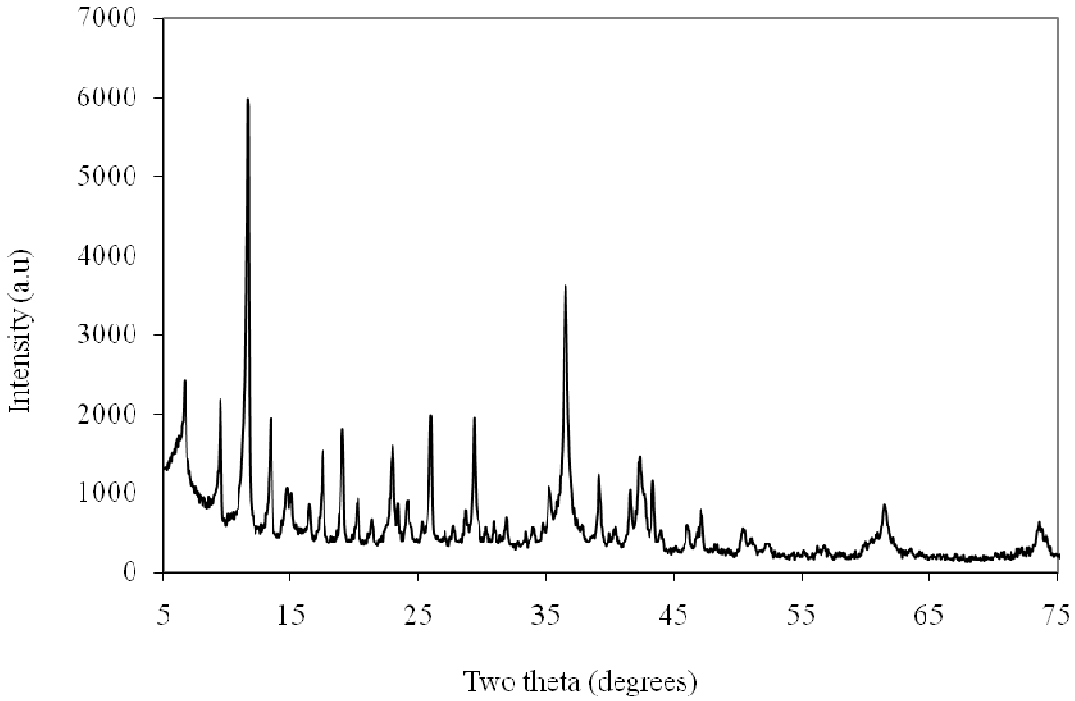

Figure 4.7: Powder XRD pattern of Cu-BTC sample

4.3 Thermal Stability

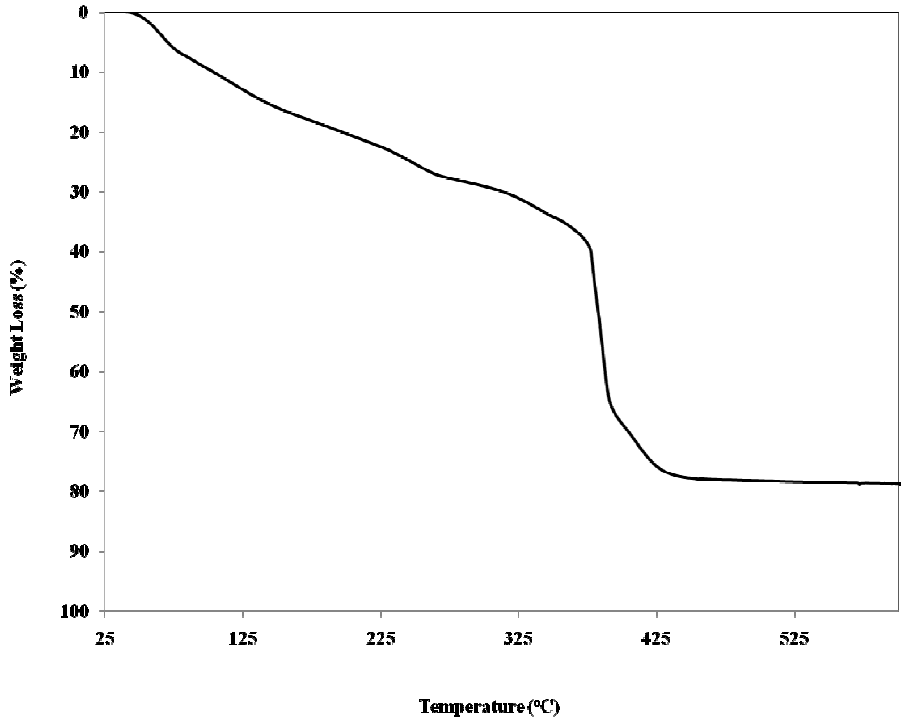

Figure 4.8: TGA pattern of Cr-BDC sample

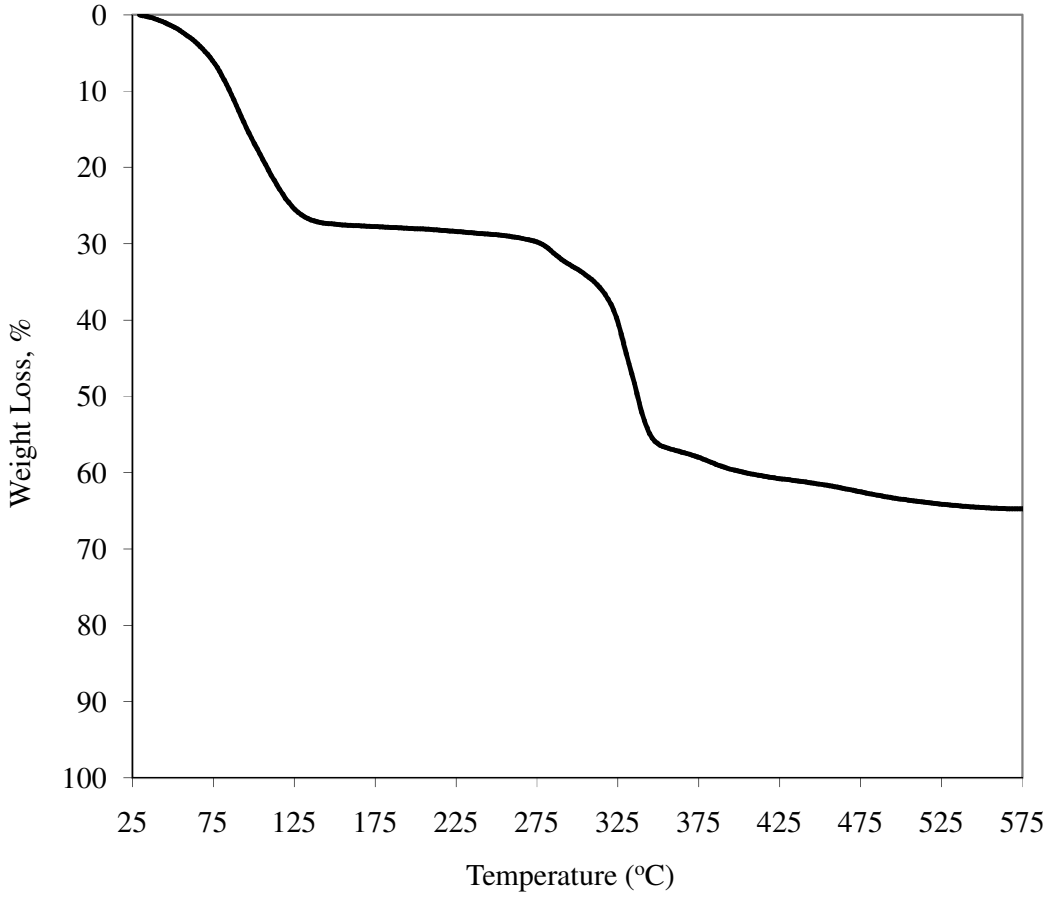

Figure 4.9: TGA pattern of Cu-BTC sample

Thermal stability of the products was characterized using a thermo-gravimetric analyzer (SHIMADZU, DTG 60 H). In both the cases about 10 mg of the samples were taken inside a 60 µL alumina crucible and was placed in a TGA and the temperature was ramped from 25°C to 600°C at a ramp of 2 °C min^{-1} in continuous air flow (45 cm^3 min^{-1}).

From TGA data, the weight loss curve for Cr-BDC has been plotted in Figure 4.8. It shows two distinct weight loss steps. The first step, in the range from 25 to 350°C corresponds to the loss of guest water molecules; the second weight loss step (350 to 600°C) is due to the elimination of OH/F groups leading to the decomposition of the framework. For any gas adsorption experiment, the true weight of the sample is taken to be the one after the initial

weight loss step at about 200^{o}C. From the TGA pattern we can fairly conclude that Cr-BDC show a very good thermal stability as compared to its counterparts.

In the same note, the weight loss pattern for Cu-BTC can be divided into 3 distinct zones. The first one between 25-125^{o}C is due to the loss of moisture or other volatile materials; the second one between 125-275^{o}C is the zone where weight remains fairly constant and for all gas adsorption study this can be treated to be range to work with. The framework collapses beyond 300^{o}C which forms the third zone.

4.4 Synthesis of other variants

In our present study we tried to experiment with the organic ligand part in synthesizing some of the derivatives of Cu and Cr based MOFs. The whole idea revolved around exploring the concepts of reticular chemistry and the ‘serendipitous’ nature of reactions. The findings of our experiments are given in the tabular form.

Table 4.1: Synthesis procedures for other variants of Cu and Cr based MOFs

Adsorbent	Synthesis Conditions		No. of batches run	Inference
	Temperature	Time		
	(degree C)	(hours)		
Cu-BDC	95-150	8-24	5	No product
Cr-BTC	140-220	8-24	5	No product

The above table summarizes all experimental conditions leading to synthesize some novel variants of Cu and Cr based metal organic frameworks. Experimental conditions were pragmatically chosen. However, none of these parings could yield any product. It is thus prudent to conclude that mere change in organic ligands don't necessarily result into a 3-D MOF structure. It is however important to mention here that 'any suitable deprotonating agent' may still result into a 3-D motif with the same combinations.

CHAPTER 5

Conclusions and Future Scope

In this present work we have successfully synthesized and characterized two very important constituents of MOF family *viz*. Cr-BDC or MIL-101 and Cu-BTC also known as KHUST-1. The scanning electron microscopy imaging of both the samples gave contrasting images whereas optical microscopy imaging for Cu-BTC helped us to ascertain the formation of certain impurities. The powder XRD pattern showed the crystallinity of the MOF samples. The TGA pattern clearly indicated that Cr-BDC is thermally more stable than Cu-BTC whereas Cr-BDC is more susceptible to ambient conditions as it adsorbs more moisture. A few newer routes were tried to synthesis some other variant of Cu and Cr based MOFs without much success. It amply illustrated that mere change in ligand and synthesis conditions don't necessary yield 3-D MOF framework.

There is a plenty of scope of this present work. It is of paramount important to actually find the surface area, pore volume and pore size distribution of all the synthesized products. Additionally, newer mechanisms are required to be invented to improve the thermal and chemical stability of synthesized materials.

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